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RESEARCH REPORT No. CX-41

The Application of Wave Functions Containing Interelectron Coordinates

I. The Ground State Energy of Lithium

PETER WALSH and SIDNEY BOROWITZ

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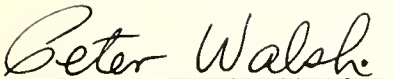
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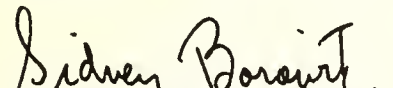
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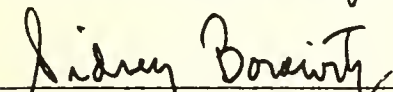
Research Report No. CX-41

THE APPLICATION OF WAVE FUNCTIONS
CONTAINING INTERELECTRON COORDINATES
I. The Ground State Energy of Lithium

Peter Walsh and Sidney Borowitz


Peter Walsh


Sidney Borowitz


Sidney Borowitz
Acting Director

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Abstract

This report treats the description of atomic systems by the novel method of introducing interelectron coordinates explicitly. The simplest atomic systems, helium and lithium, are treated and excellent results are found in calculating the energy values of the corresponding ground states. In addition, an approximation technique of high accuracy has been developed to handle, mathematically, wave functions containing many interelectron coordinates.

Table of Contents

	<u>Page</u>
1. Introduction	1
2. Scattering wave function in helium-like systems	4
3. Many-electron systems	12
4. Mathematical approximation	16
5. Energy calculation for the ground state of lithium	27
6. Results	43
Appendix I	46
Appendix II	49
References	52

1. Introduction

The problem of suitably describing atomic systems has been attacked since the advent of Quantum Theory. The statistical theory of Thomas^[1] and Fermi^[2], the self-consistent method of Hartree^[3] and the methods of Slater^[4] and Morse^[5] are among the oldest and have been widely investigated. All of these methods deal, in essence, with the nuclear coordinates of the individual electrons. Although it has long been recognized that the interelectron potential within the atom is of comparable magnitude to the nuclear potential, little work was done originally in using interelectron coordinates explicitly. The well-known variational method of Hylleraas^[6] does introduce the interelectron coordinates. However, the wave function is specified only after a variational calculation of the energy, and the method is consequently difficult to apply to excited states and to atoms much heavier than lithium. The method of configuration interaction as generalized by Löwdin^[7] and applied by Tycko, Thomas and King^[8] shows excellent promise in treating the interelectron effects although the interelectron coordinates are not introduced in a direct manner. The recent approaches of Brueckner^[9] and of Bohm and Pines^[10] which also treat interelectron effects have not found much application, as yet, in atomic systems.

A few years ago, Pluvinaige^[11] made a substantial advance in the use of interelectron coordinates in atomic systems when he illustrated how the Schroedinger Equation can be partially separated, using nuclear and interelectron coordinates together, so that the interelectron potential no longer appears as the perturbing term. In this partial separation

the perturbing term has the character of derivative terms (as it were, 'velocity dependent' potentials) and these derivative terms are always finite in space. The interelectron potentials are, of course, infinite when two electrons have zero separation. The zero order wave function for such a system becomes a product of bound state hydrogenic wave functions for the nuclear coordinates and continuum state hydrogenic wave functions of variable kinetic energy for the interelectron coordinates. Such a wave function takes into account the binding of all the electrons to the nucleus and also the mutual scattering among the electrons themselves. We will designate product wave functions of this type as scattering wave functions (SWF) to distinguish them from the product of bound wave functions (BWF) involving only the nuclear coordinates.

The SWF would be expected to yield much better results than the corresponding BWF since all of the potentials, nuclear and interelectronic, are accounted for in the SWF. This was indeed the result found by Pluvinaige when he used the SWF to obtain variational energies of ground states of helium-like systems. The SWF gave answers which were in general twice as close to the experimental results as the corresponding BWF.

The purpose of this paper is to modify and expand the Pluvinaige approach in such a way that SWF can be used with a reasonable amount of labor for atomic systems beyond the helium type. Once the modification has been accomplished the actual results will be tested in the case of the ground state of lithium.

Two things have been done in applying SWF to atomic systems beyond helium. It was first noted that the use of continuum wave functions of zero kinetic energy greatly simplifies the mathematics and allows integration of the SWF terms of tabulated functions. In Section 2 we discuss this aspect of the problem and present a comparison of the energies calculated using the simplified SWF with those of Pluvinaige in helium-like systems. In Section 3 the method for applying these simplified SWF to more complicated systems is described and it is seen that these SWF describe the nuclear coordinates as Fermi-Dirac 'particles' filling the bound energy levels pairwise, while the interelectron coordinates are described as Bose 'particles' all piling into the lowest energy continuum state.

The second thing done in applying SWF was to devise an accurate approximation method to integrate functions containing three or more interelectron coordinates over the space of the nuclear coordinates (including angles). In Section 4 an accurate approximation method is described which consists of expanding the functions containing the interelectron coordinates about well-chosen points in the space of the nuclear coordinates. The approximation technique is tested in helium-like systems and is found to be better than 99 % accurate.

In Section 5, the ground state energy for lithium is calculated using the SWF proposed and the approximation technique described. The accuracy of the approximation technique is fully maintained in lithium. The results are discussed to some degree in Section 6.

2. Scattering wave functions in helium-like systems

Pluvinage treated the problems of two electrons in the ground state of helium-like systems. The wave equation for such a two electron system is the following:

$$(2.1) \quad H\psi = \left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right] \psi = E\psi$$

using atomic units. The notation has its customary meaning. Because of the Coulomb potentials, the wave equation possesses singularities when the electronic distances, r_1 , r_2 , are zero or when the interelectron spacing, r_{12} , is zero. The unique feature of Pluvinage's approach is that he separated the Hamiltonian in such a way that the behavior of the electrons at any of the singularities is exactly correct. Consequently the effect of all the potentials, nuclear and interelectron, is taken into account to a very large extent.

If the coordinates r_1 , r_2 , r_{12} are used and symmetric states only are considered, then H becomes

$$(2.2) \quad H = -\frac{1}{2} \left(\frac{1}{r_1^2} \frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} + \frac{2}{r_{12}^2} \frac{\partial}{\partial r_{12}} r_{12}^2 \frac{\partial}{\partial r_{12}} \right) \\ - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} - \cos \theta_{1,12} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \cos \theta_{2,12} \frac{\partial^2}{\partial r_2 \partial r_{12}}$$

$$(2.3) \quad 2 \cos \theta_{i,ij} = \frac{r_i^2 - r_j^2 + r_{ij}^2}{r_i r_{ij}}$$

and $\theta_{i,ij}$ is the angle between \vec{r}_i and \vec{r}_{ij} .

This result immediately suggests that we take $H = H_0 + H'$ with the unperturbed wave equation as

$$(2.4) \quad H_0 \psi_0 = \left[-\frac{1}{2} \left(\frac{1}{r_1^2} \frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} + \frac{2}{r_{12}^2} \frac{\partial}{\partial r_{12}} r_{12}^2 \frac{\partial}{\partial r_{12}} \right) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right] \psi_0 = E_0 \psi_0.$$

The solution is the SWF

$$(2.5) \quad \psi_0 = \phi_n(r_1) \phi_n(r_2) u_k(r_{12}).$$

Here ϕ_n is the hydrogenic wave function for the n^{th} bound state of an atom whose nuclear charge is Z , u_k is the hydrogenic wave function for an electron in the continuum having an energy $k^2/2$ and scattering from a center of charge, $1/2$. The factors, $1/2$, occur because the interelectron coordinate, r_{12} , is shared by two electrons. The perturbation is now

$$(2.6) \quad H' = -\cos \theta_{1,12} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \cos \theta_{2,12} \frac{\partial^2}{\partial r_2 \partial r_{12}}.$$

H' is finite for all values of the coordinates and is small compared to H_0 at the singularities. The solution to the unperturbed problem thus represents the actual wave function exactly at all the singularities.

Pluvinaige took the SWF from Equation (2.4) and used it to calculate the energy of the ground state by substituting it in the variational expression

$$(2.7) \quad E = \frac{(\psi_0, H\psi_0)}{(\psi_0, \psi_0)} = -Z^2 + k^2 + \frac{(\psi_0, H' \psi_0)}{(\psi_0, \psi_0)} .$$

The integrals were evaluated by power series and the parameter varied was k . This resulted in the energy value, -2.873 AU, for helium. The correct energy is -2.90372 AU, while the energy obtained by using the product of bound hydrogenic wave function with variable atomic number, Z , is -2.848 AU. The SWF function yields an energy value which is closer to the true energy by a factor of two when compared to comparable BWF. This result is also true for the calculations made upon other helium-like systems.

The good energy value calculated by the Pluvinaige approach is gratifying. Even if no better energy value were found the approach deserves a great deal of consideration as a fundamentally different approach to atomic systems. The treatment of the singularities due to the potentials in the wave equation is very satisfying and lends a great deal of validity to the method.

The true wave function for the lowest state of a two electron system is expected to have nodes only when the electrons are at infinity and at the nucleus. However, the wave function (2.5) has an infinite number of nodes when $k > 0$ since u_k oscillates at large distances. On the other hand, u_0 has no nodes at any value of the argument. In addition, physical grounds

would indicate that k should be zero. If we removed the two electrons far from the nucleus, their kinetic energies would decrease and their motion relative to each other would also decrease and at an infinite distance from the nucleus they would scatter from each other with no relative motion at all.

The unperturbed wave equation for the interelectron coordinate with $k = 0$ is

$$(2.8) \quad \frac{d^2 u_0}{dr_{12}^2} + \frac{2du_0}{dr_{12}} - \frac{u_0}{r_{12}} = 0.$$

The solution of this equation is the modified Bessel-Clifford function of the first order, E_1 , which is finite at $r_{12} = 0$. Thus

$$(2.9) \quad u_0 = \frac{1}{i\sqrt{r_{12}}} J_1(2i\sqrt{r_{12}}) \equiv E_1(r_{12})$$

where J_1 is the Bessel function of first order. Tables of the Bessel-Clifford function are available [12].

The advantage of the use of the wave function, $u_0 = E_1$, for the SWF is twofold. Firstly, the integrals which contain the full wave function are integrable in closed and relatively simple form. Secondly, a physical basis has been obtained for selecting one of a set of SWF for use in problems. This obviates the need to adjust k by a variational method whenever the SWF is to be used. This second is a true advantage only if the wave function using $k = 0$ is comparable in accuracy with one using the best value of k . That this is so is shown below. The a priori selection of a

particular value of k will save a considerable amount of effort in the calculation of the energy level of the lithium ground state.

We now proceed to the calculation of the energy of the ground state of helium and helium-like ions using

$$(2.10) \quad \psi_0 = e^{-Zr_1} e^{-Zr_2} E_1(r_{12}) .$$

This will be compared with Pluvina's results as a test of the usefulness of this particular SWF. As usual the variables used by Hylleraas^[6] are best suited to the problem. Therefore, we set

$$(2.11) \quad s = r_1 + r_2 , \quad t = r_1 - r_2$$

and retain the variable r_{12} . The volume element is now

$$(2.12) \quad dt = 2\pi^2(s^2 - t^2)r_{12} ds dt dr_{12}$$

Since the ground state is symmetric, only even powers of t appear in the integrals and this results in the factor 2 appearing in the equation. It is very convenient to arrange the limits of integration in such a manner that the integration over r_{12} appears last and covers the region from zero to infinity. Thus we have

$$(2.13) \quad 0 \leq t \leq r_{12} , \quad r_{12} \leq s \leq \infty , \quad 0 \leq r_{12} \leq \infty .$$

Using the Hylleraas variables and remembering that $k = 0$, the expression for the energy becomes

$$(2.14) \quad E = -Z^2 + \frac{H'_{oo}}{N_{oo}}$$

where

$$(2.15) \quad H'_{oo} = Z(2\pi^2) \int_0^\infty dr_{12} \int_{r_{12}}^\infty ds \int_0^{r_{12}} dt s(r_{12}^2 - t^2) e^{-2Zs} \left(\frac{dE_1^2}{dr_{12}} \right)$$

$$(2.16) \quad N_{oo} = (2\pi^2) \int_0^\infty dr_{12} \int_{r_{12}}^\infty ds \int_0^{r_{12}} dt r_{12}(s^2 - t^2) e^{-2Zs} u_o^2 .$$

Since k is constant the variational expression for the energy has become the usual first order perturbation expression.

The quantities N_{oo} and H'_{oo} are evaluated by first integrating over the t and s coordinates. In the case of H'_{oo} an integration by parts is then performed and we have finally

$$(2.17) \quad H'_{oo} = 2\pi^2 Z \left(\frac{2}{3} I_4(Z) - \frac{1}{Z} I_3(Z) - \frac{1}{2Z^2} I_2(Z) \right)$$

$$(2.18) \quad N_{oo} = 2\pi^2 \frac{1}{2Z} \left(\frac{2}{3} I_4(Z) + \frac{1}{Z} I_3(Z) + \frac{1}{2Z^2} I_2(Z) \right)$$

where

$$(2.19) \quad I_n(Z) = \int_0^{\infty} e^{-2Zr_{12}} E_1^2(r_{12}) r_{12}^n dr_{12} \quad .$$

The integral, I_1 , is evaluated by integrating over the Bessel function^[13] with the substitution $r_{12} = V^2$. The expression for I_1 is

$$(2.20) \quad I_1(Z) = \frac{1}{4Z^2} \exp\left(\frac{1}{Z}\right) E_1\left(\frac{1}{4Z^2}\right) .$$

The integrals for n greater than one are obtained easily from I_1 by differentiating with respect to Z or by using certain recurrence relations. The method for doing this is discussed in Appendix I where the explicit expressions for several of the I_n are also given. These expressions are simple combinations of polynomials in Z , the exponential function and the modified Clifford-Bessel functions, E_0 and E_1 . The latter are rather fully tabulated in Reference [12]. They can also be computed from their power series representation, Equation (I.3), which converges quite rapidly.

The ground state energy was calculated for several helium-like ions and atoms by the method outlined above. Its deviation, D_S , from the experimental energy, ($D = E_{\text{calc}} - E_{\text{exp}}$) is given in Table I, in atomic units, and is compared with several other computed deviations. D_P is the deviation obtained from Pluvinaige's work, D_B is that calculated using BWF and, D_Z that calculated by BWF with variable Z .

There are several noteworthy features exhibited in Table I. The indicated superiority of the Pluinage wave function is clearly shown. That the choice of k equal to zero is indeed a good one is quite evident. A major part of the improvement in energy obtained by Pluinage is retained with k equal to zero with a substantial saving in labor. The energy value of H^- is easily calculated with k taken as zero whereas Pluinage did not calculate this energy, presumably because of the slow convergence in the power series he used. Incidentally, the energy value calculated for H^- does not quite yield binding, falling 0.002 AU short of the energy of atomic hydrogen.

Since the two electrons in the inner shell of neutral lithium contribute the major part of the energy in the ground state of lithium ($Z = 3$), the table shows that the use of E_1 in the wave function will probably yield 80 % of the improvement we can expect if we varied k . The labor saved in the process of calculating the energy of neutral lithium using E_1 will prove substantial.

$$D = E_{\text{calc}} - E_{\text{exp}} \text{ in A.U.}$$

	Z	$E_{\text{exp}}(\text{A.U.})$	D_B	D_Z	D_S	D_P
H^-	1	-0.528	0.153	0.055	0.030	-
He	2	-2.904	0.154	0.056	0.029	0.026
Li+	3	-7.280	0.155	0.057	0.031	0.025
Be ²⁺	4	-13.656	0.155	0.057	0.033	0.025
B ³⁺	5	-22.031	0.156	0.058	0.034	0.025
C ⁴⁺	6	-32.406	0.156	0.058	0.034	0.025
N ⁵⁺	7	-44.781	0.156	0.058	0.035	0.025
	∞	-	0.157	0.059	0.040	-

TABLE I.

Deviation of various calculated energy values from the experimental values of the ground state of helium-like atoms and ions. The energy differences at infinite Z are obtained by comparison with the formula given by Hylleraas and Mitdal [14] for the energy.

The advantage of using the SWF with $k = 0$, over the BWF in a perturbation-type approach to atomic wave functions is even more evident in Table I. D_B is the deviation of the first order perturbation energy from the experimental value when the interelectron distance is considered the perturbation. This deviation is four to five times the deviation calculated when the Hamiltonian is broken in such a manner that Equation (2.6) is the perturbation. This strongly indicates that excited states, which cannot be treated easily by a variational method, could be treated with good results by a perturbation approach based upon the SWF with k taken as zero.

3. Many-electron systems

In the last section we illustrated, in the case of the two-electron system, the simplification we have proposed to the Pluvillage method. The extension to the many electron case poses some problems. We cannot write down a Hamiltonian for a many electron system which is analogous to the one that has been written down for the case of helium. The easiest way to see this is to note that if we were to introduce the interelectron coordinates, the radial coordinates of each electron plus three Euler angles, the number of coordinates we have available with which to express the Hamiltonian is

$$N + N(N - 1)/2 + 3$$

where N is the number of electrons. The original number of degrees of

of freedom is $3N$. If we now insist that the total number of coordinates used to express the Hamiltonian be the same, we have that N must be equal to either 2 or 3. Thus, we could not proceed in this way for any element beyond lithium.

We can circumvent this difficulty as follows: First we are guided by our discussion of the helium problem in our choice of an approximate wave function to describe the many electron system. The generalization of the wave function which we have used for the helium atom is

$$(3.1) \quad \psi_0 = \left[D \prod_i \phi_m(r_i) \right] \prod_{\ell > n} E_1(r_{\ell n})$$

in which D represents the Slater determinant of unperturbed hydrogenic wave functions corresponding to suitable unperturbed states. The E_1 functions are the Clifford-Bessel functions of their argument. The product of the Clifford-Bessel function remains invariant as we interchange the coordinates. Thus, the total wave function is properly antisymmetric provided we include the spin wave functions in the ϕ_m . According to (3.1) we have restricted ourselves to S states since the ϕ 's depend only on the radial coordinates. The generalization to other unperturbed angular momentum states poses no essential difficulty.

The approximate energy is given by

$$(3.2) \quad (\psi_0, H \psi_0) = \int \psi_0^* H \psi_0 \overrightarrow{dr_1} \dots \overrightarrow{dr_n}$$

where H is given by

$$(3.3) \quad \left\{ -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{j > k} \sum \frac{1}{r_{jk}} \right\} \psi = E\psi$$

and the ψ_0 are properly normalized. Since the ψ_0 depends on the coordinates r_i and r_{ij} , we can reexpress the operator H in terms of the coordinates r_i and r_{ij} by the rules of partial differentiation. This decomposes H into two parts H_0 and H' , where

$$(3.4) \quad H_0 = \sum_i -\frac{1}{2} \left(\frac{1}{r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} - \frac{Z}{r_i} \right) \\ + \sum_{\ell > m} \left(-\frac{1}{r_{\ell m}^2} \frac{\partial}{\partial r_{\ell m}} r_{\ell m}^2 \frac{\partial}{\partial r_{\ell m}} + \frac{1}{r_{\ell m}} \right)$$

and

$$(3.5) \quad H' = - \sum_{i \neq j} \sum \cos \theta_{i,ij} \frac{\partial^2}{\partial r_i \partial r_{ij}} \\ - \sum_{k \neq \ell \neq m} \sum \cos \theta_{k\ell,km} \frac{\partial^2}{\partial r_{k\ell} \partial r_{km}} .$$

The effect of H_0 operating on ψ_0 in the integral is to yield a contribution to the energy equal to the sums of the hydrogenic energies of the electrons neglecting their interactions, since the use of the Clifford-Bessel functions in ψ_0 corresponds to an eigenvalue of 0 for that part of H_0 .

The corrections to the hydrogenic energies is given by

$$(3.6) \quad \int (\psi_0^* H' \psi_0) \overrightarrow{dr_1} \dots \overrightarrow{dr_2} \quad .$$

The perturbing Hamiltonian, H' , contains a new set of terms which do not appear in two electron systems. In addition to the interaction between the nuclear and the interelectron coordinates, the interaction among the interelectron coordinates now appears.

When we had to evaluate the integral similar to (3.6) for the case of helium, we expressed the volume element in terms of the coordinates, r_1 , r_2 and r_{12} , and properly restricted the range of integration. For heavier atoms expressing the volume element in terms of the interelectron coordinates is not a fruitful way to proceed. In the first place, there are too many of them and, in the second place, it is doubtful that the integrals could be carried out since the range of integration would have to be severely restricted. However, this paper will present a very accurate approximation technique for doing this in a rather simple manner and this technique will form the basis of the calculations in lithium. The lithium problem will thus serve as a testing ground for the usefulness and accuracy of the approximation technique developed.

4. Mathematical approximation

The type of integration which must be evaluated is of the following general form:

$$(4.1) \quad I(Z) = \int f(Z, r_1, r_2 \dots r_n) g(r_{12}, r_{13} \dots r_{n-1,n}) d\vec{V}.$$

The function, f , has a monotonic exponential variation in the radial direction. g also varies monotonically but more slowly than f . $d\vec{V}$ is the volume element in the space of the n electrons. The integral of f alone over all the coordinates can be performed and, in the applications we make, is simply the integral of products of hydrogenic wave functions over the corresponding radial coordinates and angles. The relatively slow variation of g compared to f leads us to expect that a Taylor expansion of g about well-chosen points in the space of all the radial coordinates and angles will lead to a rapidly convergent series of integrals to represent I . Indeed we have been able to treat the expansion in such a way that the first term alone gives an answer which is generally more than 99 % accurate for the type of integrals with which we must deal. Such accuracy will give an answer for the energy of the lithium ground state with a computational error much smaller than the expected difference between the computed energy and the experimental energy.

The scheme adopted to evaluate I is as follows: Expand g about the radial points $r_{10}, r_{20} \dots r_{n0}$ thus

$$(4.2) \quad g(r_{12}, r_{13} \dots r_{n-1,n}) = g_0 + \sum_{i=1}^n \left. \frac{\partial g}{\partial r_i} \right|_{r_i = r_{i0}} (r_i - r_{i0}) + \dots$$

where g_0 indicates g evaluated at the radial expansion points. Since we have not expanded g in terms of the angles, g_0 and $\left. \frac{\partial g}{\partial r_i} \right|_{r_i = r_{i0}}$ are, as yet, functions of the various angular coordinates. Substitute Equation (4.2) into (4.1); then there results

$$(4.3) \quad I(Z) = \int \dots \int f g_0 d\vec{V} + \sum_{i=1}^n \int f \left. \frac{\partial g}{\partial r_i} \right|_{r_i = r_{i0}} (r_i - r_{i0}) d\vec{V} + \dots$$

To speed the convergence of the series the r_{i0} are chosen such that the second terms in the series are zero. Thus the formulas for the r_{i0} are

$$(4.4) \quad \int_0^\infty f \times (r_i - r_{i0}) d\vec{V} = 0 ; \quad i = 1, \dots, n .$$

The separation of the angular and radial coordinates allowed $\left. \frac{\partial g}{\partial r_i} \right|_{r_{i0}}$ to be taken outside of the integral.

After the r_{i0} have been determined the angular expansion points are then found. The angular treatment is different from the radial treatment for two reasons. First, the angular variation, which appears in the term $f d\vec{V}$, is generally slow or only comparable to the variation that occurs in g . Second, the radial treatment depends only on the value of g and not its shape, since $\frac{\partial g}{\partial r_i}$ does not appear explicitly in determining r_{i0} or I . We make use of the angular treatment to introduce the shape of g . The criterion established to determine the angular coordinates θ_{i0}, α_{i0} is then this: The angles are chosen to be those angles for which the integrand has a maximum subject to Equations (4.4).

It is more convenient to deal with the logarithm of the integrand;
therefore,

$$(4.5) \quad \frac{\partial}{\partial \theta_i} \left[\ln \left\{ w_i(\theta_i) g_o \right\} \right] = 0$$

$$\frac{\partial}{\partial \theta_j} \left[\ln \left\{ w_j(\theta_j) g_o \right\} \right] = 0$$

w is the appropriate weighting function for the angle which appears in the volume element.

The system of Equations (4.5) must be solved simultaneously, and in practice an iteration procedure is used to solve them. Since the inter-electron coordinates which enter into g do not depend strongly upon the angles, the iteration of Equations (4.5) converges quite rapidly if a reasonable guess is originally made for the angles.

Writing r_{ijo} as the value of r_{ij} at r_{io} , θ_{io} , α_{io} we now have for I

$$(4.6) \quad I^A(Z) = g(r_{120}, r_{130}, \dots, r_{n-1, no}) \int f(Z, r_1, r_2, \dots, r_n) d\vec{V}.$$

Note the dependence of I upon Z in Equations (4.1) and (4.6). With large Z the exponential variation of f is so strong that only those regions near the nucleus contribute to I. As long as g is monotonic this means that Equation (4.1) reduces to

$$(4.7) \quad I(\infty) = g(o, o, \dots, o) \int \dots \int f d\vec{V}.$$

This is exactly the form which Equation (4.6) assumes at large Z and that expression is thus exact at Z equal to infinity.

The approximate expression for I can be modified in several ways of special importance. For example, it sometimes happens that g is not monotonic or uniquely defined when all interelectron coordinates are zero. However, it may be possible to separate g into two parts, one of which is monotonic and uniquely defined at zero interelectron distances and the remaining function is directly integrable. Thus

$$(4.8) \quad g = G\chi$$

where χ is integrable. Then, in the same manner as previously,

$$(4.9) \quad I^A(Z) = G(r_{120}, \dots) \int \chi d\vec{V}$$

still subject to Equation (4.4). This expression is exact at $Z = \infty$. Other modifications are also possible. For instance, χ may be integrable when the r_{i0} are determined, or perhaps it is not integrable at all. In these two cases equations paralleling (4.6) and (4.9) are easily written; however, they are not correct at $Z = \infty$. To make them correct, the equations can be multiplied by a constant which equals the ratio of the approximate to the true answer as Z approaches infinity.

The accuracy of the method described above will be illustrated by using it to calculate the normalization integral N_{00} and the perturbing Hamiltonian integral, H'_{00} , for helium-like systems and comparing with the exact results given by Equations (2.16) and (2.17).

The normalization integral is:

$$(4.10) \quad N_{oo} = \int \int e^{-2Z(r_1+r_2)} E_1^2(r_{12}) d\vec{r}_1 d\vec{r}_2$$

where

$$f = e^{-2Z(r_1+r_2)}, \quad g = E_1^2(r_{12})$$

Take r_1 as a polar axis and let θ_2 be the azimuthal angle between r_2 and r_1 . The integrals over all the orientations of r_1 and over the polar angle, ϕ_2 , or r_2 can be performed immediately. This results in

$$(4.11) \quad N_{oo} = 8\pi^2 \int_0^\infty \int_0^\infty \int_0^\pi e^{-2Z(r_1+r_2)} E_1^2(r_{12}) r_1^2 dr_1 r_2^2 dr_2 \sin \theta_2 d\theta_2$$

where now

$$r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}$$

The radial expansion points are determined by Equation (4.4) yielding

$$(4.12) \quad r_{10} = r_{20} = \frac{3}{2Z}$$

The angular expansion points reduce to the single point, θ_{20} , determined by Equation (4.5) in the form

$$(4.13) \quad \frac{\partial}{\partial \theta_2} \left[\ln \left\{ \sin \theta_2 E_1^2(r_{10}, r_{20}, \theta_2) \right\} \right]$$

Set

$$(4.14) \quad \phi^0 = \frac{r_{120}}{E_1^2} \left. \frac{dE_1^2}{dr_{12}} \right|_{r_{120}}$$

$$= 2 \left[\frac{E_0(r_{120})}{E_1(r_{120})} - 1 \right]$$

where we have used Equation (I.4) of the Appendix. Thus

$$(4.15) \quad \cos \theta_{20} = - \frac{\phi^0}{2 + \phi^0} = \frac{E_1}{E_0} - 1$$

and

$$(4.16) \quad r_{120} = \sqrt{2} r_{10} \sqrt{2 - E_1/E_0}$$

where E_0 and E_1 are evaluated at r_{120} . Using this value of r_{120} and integrating over the exponential, the formula (4.6) becomes

$$(4.17) \quad N_{oo}^A = (\pi^2/Z^6) E_1^2(r_{120}).$$

The evaluation of r_{120} from (4.16) is obtained by a series of iterations, which as mentioned already, converges rapidly. Two iterations generally yield r_{120} to an accuracy of a part per thousand with a fair estimate for θ_{20} or r_{120} initially.

The quantity E_1^2 is a direct measure of the change produced in the normalization integral because of the presence of the interelectron term in the wave function. A comparison of the approximate answer for the normalization integral with the exact is made in Table II where $E_1^2 = Z^6 N_{oo}^A / \pi^2$ is tabulated versus $Z^6 N_{oo}^{Ex} / \pi^2$ for various values of Z . Except for $Z = 1$, the error is less than one percent despite the fairly large change produced by the presence of the interelectron term. The interelectron term is clearly not a small perturbation even at Z as large as 6. The excellent accuracy throughout the entire range is quite gratifying; at $Z = 1$, the error is less than 6 % despite the increase of almost 9 times in the normalization integral.

The integral, H_{oo}' , is obtained from (2.6) by integration. It is convenient for the present case to differentiate with respect to the radial coordinates and then to combine the angular terms by using Equation (2.3). Establishing r_1 as the polar axis and integrating over the orientations of r_1 and the polar angle of r_2 as before, yields:

$$(4.18) \quad H_{oo}' = (8\pi^2)Z \int_0^\infty \int_0^\infty \int_0^\pi \left[e^{-2Z(r_1+r_2)} (r_1 + r_2) (1 - \cos \theta_2) \right. \\ \left. \times \frac{1}{r_{12}} \frac{dE_1^2}{dr_{12}} r_1^2 dr_1 r_2^2 dr_2 \sin \theta_2 d\theta_2 \right] .$$

The function f is the same as before but g has the form

$$(4.19) \quad g = \frac{(r_1 + r_2)(1 - \cos \theta_2)}{r_{12}} \frac{du_o^2}{dr_{12}}.$$

Because of the angular term, g is not uniquely defined at $r_{12} = 0$. We thus try Equation (4.8) where

$$(4.20) \quad G = \frac{dE_1^2}{dr_{12}}, \quad \chi = \frac{(r_1 + r_2)(1 - \cos \theta_2)}{r_{12}}$$

and we find that χ is indeed integrable.

As before $r_{10} = r_{20} = 3/2Z$. However, the angle θ_{20} is now changed and is given by

$$(4.21) \quad \frac{\partial}{\partial \theta_2} \left[\ln \left\{ \left(\frac{dE_1^2}{dr_{12}} \right) \frac{(1 - \cos \theta_2)}{r_{12}} \sin \theta_2 \right\} \right] = 0$$

evaluated at r_{10}, r_{20} .

Setting

$$(4.22) \quad \phi' = \frac{dE_1^2}{dr_{12}} = \frac{2E_1(E_0 - E_1)}{r_{12}}$$

$$\begin{aligned} \phi' &= \frac{r_{120}}{\phi} \left. \frac{d\phi}{dr_{12}} \right|_{r_{120}} \\ &= \frac{r_{120} + [(E_0/E_1) - 1][(E_0/E_1) - 1]}{[(E_0/E_1) - 1]} \end{aligned}$$

we have

$$(4.23) \quad \cos \theta_{20} = - \frac{(2 + \phi')}{(4 + \phi')}$$

and

$$(4.24) \quad r_{120} = 2r_{10} \sqrt{\frac{3 + \phi'}{4 + \phi'}}$$

The quantities E_0, E_1 entering into ϕ are evaluated at r_{120} . Once r_{120} is obtained by iteration, Equation (4.9) then gives

$$\begin{aligned} (4.25) \quad H_{00}'^A &= (8\pi^2)(2Z) \frac{E_0(E_0 - E_1)}{r_{120}} \iiint e^{-2Z(r_1 + r_2)} \\ &\times \frac{(r_1 + r_2)(1 - \cos \theta_2)}{r_{12}} r_1^2 dr_1 r_2^2 dr_2 \sin \theta_2 d\theta_2 . \end{aligned}$$

The remaining integration can be done in several ways. It is simplest to use the Hylleraas variables. The integral then becomes

$$\frac{1}{4} \int_0^{\infty} dr_{12} \int_{r_{12}}^{\infty} ds \int_0^{r_{12}} dt s(r_{12} - t) e^{-2Zs}$$

which is easily evaluated and equals $5/(2Z)^6$. Finally,

$$(4.26) \quad H_{oo}^{'A} = \frac{E_o(E_o - E_1)}{r_{120}} \left(\frac{5}{4} \frac{\pi^2}{Z^5} \right).$$

Table II presents a comparison of approximate and exact values of $H_{oo}^{'A}$ for various Z . The error is again less than one percent although larger than in the case of the normalization integral.

Z	$\left(\frac{Z^6}{\pi^2}\right) N_{oo}^{Ex}$	$\left(\frac{Z^6}{\pi^2}\right) N_{oo}^A$	$\frac{N_{oo}^A}{N_{oo}^{Ex}}$	$\left(\frac{4Z^5}{5\pi^2}\right) H_{oo}^{'Ex}$	$\left(\frac{4Z^5}{5\pi^2}\right) H_{oo}^{'A}$	$\frac{H_{oo}^{'A}}{H_{oo}^{'Ex}}$
1	9.458 ₇	8.931 ₂	0.944 ₂	3.802 ₀	3.444 ₁	0.906 ₀
2	3.053 ₇	3.075 ₈	1.007 ₂	1.370 ₉	1.360 ₈	0.992 ₁
3	2.093 ₇	2.111 ₄	1.008 ₅	0.977 ₈	0.980 ₉	1.003 ₁
4	1.737 ₉	1.746 ₅	1.005 ₀	0.826 ₃ ₀	0.8305 ₇	1.005 ₂
5	1.555 ₅	1.558 ₆	1.002 ₅	0.7470 ₆	0.7510 ₃	1.005 ₃
6	1.443 ₈	1.445 ₀	1.000 ₈	0.6982 ₈	0.7020 ₅	1.005 ₄
7	1.369 ₆	1.369 ₃	0.999 ₈	0.6658 ₈	0.6690 ₀	1.004 ₇

TABLE II.

Comparison of approximate values, N_{oo}^A , $H_{oo}^{'A}$ with exact values, N_{oo}^{Ex} , $H_{oo}^{'Ex}$

Before closing this section, we will indicate the way in which the approximation technique will be applied in lithium. The function E_1 recommends itself because it is readily integrable. To obtain the best accuracy possible in lithium consistent with a reasonable amount of labor we will always integrate over one of the interelectron coordinates as well as the radial coordinates. To see how this is to be done the differential element of volume is examined. Choosing one electronic vector, say \vec{r}_3 , as the polar axis and denoting $\theta_1, \theta_2, \phi_2$ as the azimuthal angles of \vec{r}_1, \vec{r}_2 with respect to \vec{r}_3 and the polar angle of \vec{r}_2 with respect to a plane through \vec{r}_1 and \vec{r}_3 , we easily see that

$$(4.27) \quad d\vec{V} = 8\pi^2 r_1^2 dr_1 r_2^2 dr_2 r_3^2 dr_3 \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 d\phi_2 .$$

We now choose r_{12} as one of the integration variables. From

$$r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 (\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi_2)} \quad \text{we obtain}$$

$$(4.28) \quad d\vec{V} = 8\pi^2 r_1 dr_1 r_2 dr_2 r_3^2 dr_3 r_{12} dr_{12} \frac{d\theta_1 d\theta_2}{\sin \phi_2} .$$

In conformity with the previous discussions $r_{10}, r_{20}, r_{30}, r_{120}$ are chosen by

$$(4.29) \quad \int f \times (r_i - r_{i0}) d\vec{V} = 0 \quad i = 1, 2, 3$$

$$\int f \times (r_{12} - r_{120}) d\vec{V} = 0 .$$

To choose the angular expansion points, we note that there is a singularity in the integral in the ϕ_2 direction at $\phi_2 = 0, \pi$ because of the volume element (4.28). In practice the $\phi_2 = \pi$ value which places \vec{r}_1 and \vec{r}_2 farthest away from each other gives the largest value in the vicinity of the singularity. We thus take

$$(4.30) \quad \phi_{20} = \pi .$$

θ_{10} and θ_{20} are now determined by the condition analagous to (4.5), that is,

$$(4.31) \quad \frac{\partial}{\partial \theta_1} (\ln g) = 0 ; \quad \frac{\partial}{\partial \theta_2} (\ln g) = 0$$

subject to Equations (4.29) and (4.30). As mentioned an iteration procedure is used to solve both equations in (4.31) simultaneously.

5. Energy calculation for the ground state of lithium

The wave function for the ground state of lithium follows from Equation (3.6). The two core electrons in lithium will be in the (1S) hydrogenic state and the outer electron will be in the (2S) hydrogenic state. The interelectron wave functions are all of the same form. The determinant indicated in (3.6) is then formed remembering that proper spin functions must be included. Using the symmetry properties of the Hamiltonian and of the spin functions^[15], the wave function reduces to the following

form for calculating the energy

$$\begin{aligned}
 (5.1) \quad \Phi &= e^{-Zr_1} \left\{ e^{-Zr_2} e^{-\frac{Z}{2}r_3} \left(1 - \frac{Z}{2}r_3\right) - e^{-Zr_3} e^{-\frac{Z}{2}r_2} \left(1 - \frac{Z}{2}r_2\right) \right\} \\
 &\quad \times E_1(r_{12}) E_1(r_{23}) E_1(r_{31}) \\
 &= \Phi(1,2,3) - \Phi(1,3,2) .
 \end{aligned}$$

Exchange effects occur because of the interaction of the first and second terms on the right.

The energy is obtained from Equations (3.2) and (3.3). For the ground state of lithium the energy is

$$(5.2) \quad E = \frac{-9Z^2}{8} - \frac{(M_{n,e} + M_{e,e})}{N}$$

$$N = \iiint \Phi^2 d\vec{r}_1 d\vec{r}_2 d\vec{r}_3$$

$$(5.3) \quad M_{n,e} = \sum_{i+j} \sum M_{i,ij} = \sum_{i \neq j} \sum \int \Phi \cos \Theta_{i,ij} \frac{\partial^2 \Phi}{\partial r_i \partial r_{ij}} d\vec{V}$$

$$M_{e,e} = \sum_{k \neq l} \sum_{l \neq m} \sum M_{k,l,km}$$

$$= \sum_{k \neq l} \sum_{l \neq m} \sum \int \Phi \cos \Theta_{k,l,km} \frac{\partial^2 \Phi}{\partial r_{kl} \partial r_{km}} d\vec{V} .$$

$M_{n,e}$ expresses the coupling of the interelectron and nuclear coordinates and is much larger than $M_{e,e}$ which expresses interelectron-interelectron coupling. In the usual manner the M 's and N can be split into two parts, one of which expresses the direct interactions while the other expresses the exchange or overlap effects. Thus

$$N = N^D - N^E$$

$$M_{i,ij} = M_{ijij}^D - M_{ijij}^E$$

$$M_{k\ell,km} = M_{k\ell,km}^D - M_{k\ell,km}^E$$

where

$$(5.5) \quad N^D = 2 \int \int \int \bar{\Phi}^2(1,2,3) d\vec{V}$$

$$N^E = 2 \int \int \int \bar{\Phi}(1,2,3) \bar{\Phi}(1,3,2) d\vec{V}$$

$$M_{i,ij}^D = \int \int \int \cos \theta_{i,ij} \frac{\partial^2 \{\bar{\Phi}^2(1,2,3)\}}{\partial r_i \partial r_{ij}} d\vec{V}$$

$$M_{i,ij}^E = \int \int \int \cos \theta_{i,ij} \frac{\partial^2 \{\bar{\Phi}(1,2,3) \bar{\Phi}(1,3,2)\}}{\partial r_i \partial r_{ij}} d\vec{V}$$

$$M_{k\ell,km}^D = \int \int \int \cos \theta_{k\ell,km} \frac{\partial^2 \{\bar{\Phi}(1,2,3)\}}{\partial r_{k\ell} \partial r_{km}} d\vec{V}$$

$$M_{k\ell,km}^E = \int \int \int \cos \theta_{k\ell,km} \frac{\partial^2 \{\bar{\Phi}(1,2,3) \bar{\Phi}(1,3,2)\}}{\partial r_{k\ell} \partial r_{km}} d\vec{V} .$$

Note that the derivatives act explicitly on the coordinates indicated in the differentiation. After differentiating, the r_{ij} must be expressed in terms of \vec{r}_i and \vec{r}_j and the integration performed. The integration is done approximately in the manner outlined in the previous section by integrating one of the r_{ij} variables along with the remaining radial and angular coordinates. The integrals in the M's and in N contain polynomials in their integrands. The approximation technique is applied term by term to the polynomials in order to retain the greatest accuracy.

The actual integrations will be illustrated in several cases. When written in full N^D has the form

$$(5.6) \quad N^D = \int e^{-2Z(r_1 + r_2)} e^{-Zr_3} \left(1 - Zr_3 + \frac{Z^2}{4} r_3^2\right) E_1^2(r_{12}) E_1^2(r_{23}) \\ \times E_1^2(r_{31}) d\vec{V}.$$

The interelectron variable chosen for integration connects the radial variables which have the same exponential dependence. The choice is r_{12} in this case. The Hylleraas variables can now be used to perform the necessary integrations. Take the first integral on the right as an example. There

$$(5.7) \quad f = e^{-2Zs} E_1(r_{12})$$

$$g = E_1^2(r_{23}) E_1^2(r_{31})$$

$$d\vec{V} = 8\pi^3 (s^2 - t^2) r_{12} ds dt dr_{12} r_3^2 dr_3.$$

Now

$$(5.8) \quad \int e^{-2Z(r_1 + r_2)} E_{12}^2(r_{12})(r_1 - r_{10}) d\vec{V} = 0$$

$$\therefore r_{10} = -\frac{1}{2} \frac{1}{N_{00}} \frac{d}{dZ} N_{00}$$

where N_{00} is evaluated as before and the derivative is readily performed using Equations (I.1) and (I.2) in the Appendix. We note $r_{20} = r_{30}$.

For $Z = 3$, $r_{10} = r_{20} = 0.56230$. r_{30} is given simply by

$$(5.9) \quad \int e^{-Zr_3} (r_3 - r_{30}) d\vec{V} = 0 ; \quad r_{30} = \frac{3}{Z} = 1.00000 .$$

The formula for r_{120} is

$$(5.10) \quad \int e^{-2Z(r_1 + r_2)} E_{12}^2(r_{12})(r_{12} - r_{120}) d\vec{V} = 0$$

$$r_{120} = \frac{(2\pi^2)}{N_{00}} \int e^{-2Z(r_1 + r_2)} E_{12}^2 r_{12}^2 (s^2 - t^2) ds dt du$$

$$= \frac{(2\pi^2)}{N_{00}} \left\{ \frac{1}{2Z} \left(\frac{2}{3} I_5(Z) + \frac{1}{Z} I_4(Z) + \frac{1}{2Z^2} I_3(Z) \right) \right\}$$

$$= 0.86592 .$$

The angles are determined easily in this case by symmetry. $\phi_2 = \pi$ as was shown in the previous section. Thus r_1, r_2, r_3 are situated in one plane and the angles θ_1, θ_2 of r_1 and r_2 with respect to r_3 will be equal at the extrema of the integrand, since the integrand is unchanged with the interchange of θ_1, θ_2 .

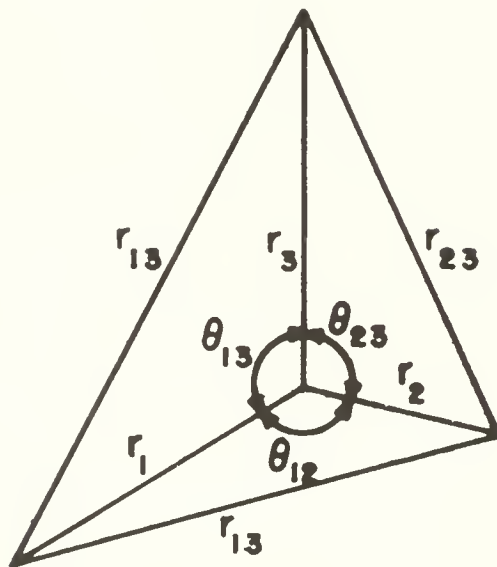


FIGURE 1.

Configuration of three electrons in a plane, illustrating various distances and angles.

Figure 1 displays the general configuration in space. When $\theta_{10} = \theta_{20}$ and $r_{10} = r_{20}$ the distances r_{120}, r_{230} are obtained immediately.

$$(5.11) \quad r_{130}^2 = r_{230}^2 = \left[r_{30}^2 + \left\{ r_{20}^2 - \left(\frac{r_{120}^2}{2} \right) \right\} \right] + \left(\frac{r_{120}^2}{2} \right)^2$$

$$r_{130} = r_{230} = 1.4264 \quad .$$

Hence

$$(5.12) \quad \int e^{-2Z(r_1 + r_2)} e^{-Zr_3} E_1^2(r_{12}) E_1^2(r_{23}) E_1^2(r_{31}) d\vec{V} \\ \cong 4\pi E_1^4(1.4264) N_{00} \frac{2!}{(3Z)^3} .$$

The other integrals in N^O are evaluated in the same manner. The only change which occurs is the change in r_{30} which takes on values $(4/Z)$, $(5/Z)$ in the two remaining integrals respectively.

The overlap integral N^E has the form

$$(5.13) \quad N^E = \int e^{-2Zr_1} e^{-3Z(r_2 + r_3)/2} \left(1 - \frac{Z}{2} (r_2 + r_3) + \frac{Z^2}{4} r_2 r_3 \right) \\ \times E_1^2(r_{12}) E_1^2(r_{23}) E_1^2(r_{31}) d\vec{V} .$$

The interelectron distance is chosen to be r_{23} . The Hylleraas variables are again introduced, and the integrals dealt with individually. The only point to note is that the I_n must now be evaluated at a new value, Z' , given by $Z' = \frac{3}{4} Z = 2.25$. The value r_{10} does not change in the different integrals while $r_{20} = r_{30}$, r_{230} do. The quantities r_{130} , r_{120} are again equal and are obtained by the symmetry properties used in N^D . One point of significance will be noted here. The second integral on the right includes the term $(r_2 + r_3)$. The greatest accuracy is found when each term is treated independently by splitting this second integral into two integrals.

The r_{20} , r_{30} are no longer equal in each integral and symmetry is then lacking. However, in calculating N^E the term $(r_2 + r_3)$ was treated as one unit since N^E is quite small compared to N^D . Several cases are illustrated below in which terms like the one described must be split up.

The method used in treating $M_{n,e}$ is now illustrated. Actually there are two methods of dealing with $M_{n,e}$. The first follows the approximation technique outlined for H_{oo}^I in Section 4. The second makes use of integration by parts under the integral sign to convert $M_{n,e}$ into integrals of the type appearing in N . The integration by parts, however, has the effect of producing very large cancellation among the resulting integrals so that the answer sought is much smaller than the integrals themselves. This second method is thus highly inaccurate. However, the comparison of answers given by both methods furnishes a valuable internal check on the accuracy of the approximation technique as used in lithium.

We illustrate the first method as applied to M^D . It is convenient to combine terms having the same value of i, j and to treat these together. Take $M_{1,12}^D + M_{2,12}^D$ as an example. Using Equations (5.5) and (2.3) the integrals combine so that

$$\begin{aligned}
 (5.14) \quad M_{1,12}^D + M_{2,12}^D &= Z \int e^{-2Z(r_1 + r_2) - Zr_3} \frac{(r_1 + r_2)}{r_{12}} (1 - \cos \theta_{12}) \\
 &\times \left((1 - Zr_3 + \frac{Z^2 r_3^2}{4}) \left[\frac{d}{dr_{12}} E_1^2(r_{12}) \right] E_1^2(r_{23}) E_1^2(r_{31}) d\vec{V} \right).
 \end{aligned}$$

Take the first integral on the right. The interelectron variable chosen for integration is, of course, r_{12} . Then the Hylleraas variables are introduced and

$$(5.15) \quad f = e^{-2Z(r_1 + r_2)} \frac{d}{dr_{12}} E_1^2(r_{12})$$

$$g = E_1^2(r_{23}) E_1^2(r_{31}).$$

The expansion points are determined in a manner similar to N^D . For example,

$$(5.16) \quad r_{10} = -\frac{1}{2H_{00}} \frac{dH_{00}}{dZ}.$$

Thus $r_{10} = r_{20} = 0.55626$, $r_{30} = 1.00000$, $r_{120} = 0.91605$. The angle ϕ_{20} is π , while θ_{10} , θ_{20} are given by symmetry so that Equation (5.11) holds and $r_{130} = r_{230} = 1.3932$.

Finally,

$$(5.17) \quad \int e^{-2Z(r_1 + r_2) - Zr_3} \frac{(r_1 + r_2)}{r_{12}} (1 - \cos \theta_{12}) \left[\frac{d}{dr_{12}} E_1^2(r_{12}) \right]$$

$$\times E_1^2(r_{23}) E_1^2(r_{31}) d\vec{V} \cong 4\pi E_1^4(1.3932) H_{00}' \frac{2!}{(3Z)^3}.$$

The same procedure applies to the other integrals in $M_{1,12}^D + M_{2,12}^D$.

The other terms in M^D do not yield quite so easily to the calculation, but they involve no essential difficulty. As an example, we take

$$(5.18) \quad M_{2,23}^D + M_{3,23}^D = M_{1,13}^D + M_{3,13}^D$$

$$\begin{aligned} M_{2,23}^D + M_{3,23}^D &= Z \int e^{-2Z(r_1 + r_2) - Zr_3} \left[\frac{d}{dr_{23}} E_1^2(r_{23}) \right] E_1^2(r_{12}) E_1^2(r_{31}) \\ &\times \left\{ \frac{(r_2 + r_3)(1 - \cos \theta_{23})}{r_{23}} \left(1 - Zr_3 + \frac{Z^2}{4} r_3^2 \right) \right. \\ &\left. + \frac{(r_3 - r_2 \cos \theta_{23})}{r_{23}} \left(\frac{Z}{4} r_3 - \frac{Z^2 r_3^2}{8} \right) \right\} d\vec{V} . \end{aligned}$$

The calculation of the integral

$$\begin{aligned} (5.19) \quad &\int e^{-2Z(r_1 + r_2) - Zr_3} \frac{(r_3 - r_2 \cos \theta_{23})}{r_{23}} \left(\frac{Z}{4} r_3 \right) \\ &\times \left[\frac{d}{dr_{23}} E_1^2(r_{23}) \right] E_1^2(r_{12}) E_1^2(r_{31}) d\vec{V} \end{aligned}$$

will be illustrated and the other terms may be found in an analogous manner.

Here

$$(5.20) \quad f = \frac{Z}{4} e^{-2Z(r_1 + r_2)} e^{-Zr_3} E_1^2(r_{12}) r_3$$

$$g = G\chi = \frac{(r_3 - r_2 \cos \theta_{23})}{r_{23}} \left[\frac{d}{dr_{23}} E_1^2(r_{23}) \right] E_1^2(r_{31})$$

where

$$\chi = \frac{(r_3 - r_2 \cos \theta_{23})}{r_{23}} \quad ; \quad G = \left[\frac{d}{dr_{23}} E_1^2(r_{23}) \right] E_1^2(r_{31}) .$$

The expansion points $r_{10} = r_{20}$, r_{30} , r_{130} are obtained from Equation (4.29), with the above formula for f . χ is integrable once the r_{10} are obtained.

Since the r_{23} and r_{13} variables do not enter into g symmetrically, we cannot use the results given earlier to determine the angles. To obtain the angles and thus r_{230} , r_{130} , we arrange r_{10} , r_{20} , r_{30} in a plane as before. Noting that $\theta_{230} = \theta_{310} + \theta_{120}$ where

$$(5.21) \quad \cos \theta_{120} = \frac{r_{120}^2 - r_{10}^2 - r_{20}^2}{2r_{10}r_{20}} .$$

The maximum of $\ln g$ with respect to θ_{23} can be obtained. This yields

$$(5.22) \quad \tan \theta_{230} = \frac{\sin \theta_{120}}{\chi + \cos \theta_{120}}$$

where

$$(5.23) \quad \gamma = \frac{r_{10}^2 r_{30}}{r_{130}^2} \frac{1}{\Phi^0(r_{130})} \left[\left(\Phi'(r_{230}) - 1 \right) \frac{r_{20}^2 r_{30}}{r_{230}^2} - \frac{1}{\cos \theta_{230} - (r_{30}/r_{20})} \right]$$

where Φ^0 and Φ' are given by Equations (4.14) and (4.22). Iteration is used to solve these two equations simultaneously starting with assumed values of θ_{230} , θ_{130} . The calculations can be set up to proceed quite rapidly on a desk calculator. Once r_{230} and r_{130} are determined, the integral in (5.19) is taken as

$$(5.24) \quad C \frac{Z}{4} E_1^2(r_{130}) \frac{d}{dr_{230}} E_1^2(r_{230}) \left(\int e^{-2Z(r_1+r_2)} e^{-Zr_3} E_1^2(r_{12}) d\vec{r}_1 d\vec{r}_2 r_3^3 dr_3 \right) \\ \times \left(2\pi \int \frac{(r_{30} - r_{20} \cos \theta_{23})}{r_{230}} \sin \theta_{23} d\theta_{23} \right)$$

where

$$(5.25) \quad C = \frac{\int e^{-2Z(r_1+r_2)} e^{-Zr_3} r_3 \frac{(r_{20} - r_{30} \cos \theta_{23})}{r_{230}} d\vec{V}}{\int e^{-2Z(r_1+r_2)} e^{-Zr_3} r_3 \frac{(r_{20} - r_{30} \cos \theta_{23})}{r_{230}} d\vec{V}}$$

is the ratio of approximate to exact r_{230} values as $Z \rightarrow \infty$.

The integrations involved in the above are facilitated through the relations:

$$\begin{aligned}
 (5.26) \quad \Theta_{ij} &= \int_0^\pi \frac{(r_i - r_j \cos \theta_{ij})}{r_{ij}} \sin \theta_{ij} d\theta_{ij} \\
 &= 2 - \frac{2}{3} \left(\frac{r_j}{r_i} \right)^2 \quad r_j \leq r_i \\
 &= \frac{4}{3} \frac{r_i}{r_j} \quad r_j \geq r_i .
 \end{aligned}$$

The integral in the denominator of Equation (5.25) is given immediately by Equation (5.26). The integral in the numerator involves further integrations. It is evaluated by splitting the range of integration of r_2 or r_3 and integrating in the usual manner. The results are straightforward although tedious and involve integrals of the type

$$\begin{aligned}
 (5.27) \quad J_n(x) &= \int_x^\infty x^n e^{-2Zx} dx \\
 &= -e^{-2Zx} \left(\frac{x^n}{2Z} + \frac{nx^{n-1}}{(2Z)^2} + n(n-1) \frac{x^{n-2}}{(2Z)^3} + \dots + \frac{n!}{(2Z)^n} \right) .
 \end{aligned}$$

The remainder of the integrals in $M_{2,23}^D + M_{3,23}^D$ are found in a similar manner and $M_{n,e}^D$ can then be evaluated. An alternate expression for this sum is obtained from Equation (II.4) in Appendix II.

In lithium this yields

$$\begin{aligned}
 (5.28) \quad M_{n,e}^D &= \int E_1^2(r_{12}) E_1^2(r_{23}) E_1^2(r_{31}) \left[\left\{ \frac{9}{8} Z^2 - Z \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right) \right\} \right. \\
 &\quad \times \left. \left\{ 1 - Z r_3 + \frac{Z^2 r_3^2}{4} \right\} + \frac{Z^2}{2} \left\{ 3 - \frac{5}{2} Z r_3 + \frac{9}{16} Z^2 r_3^2 \right\} \right] \\
 &\quad \times e^{-2Z(r_1 + r_2)} e^{-Z r_3} d\vec{V}
 \end{aligned}$$

and also

$$\begin{aligned}
 (5.29) \quad M_{n,e}^E &= \int E_1^2(r_{12}) E_1^2(r_{23}) E_1^2(r_{31}) \left[\left\{ \frac{9}{8} Z^2 - Z \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right) \right\} \right. \\
 &\quad \times \left\{ 1 - Z \frac{(r_2 + r_3)}{2} + \frac{Z^2}{4} r_2 r_3 \right\} + \frac{Z^2}{2} \left\{ 3 - \frac{5}{4} Z (r_2 + r_3) \right. \\
 &\quad \left. \left. + \frac{1}{2} Z^2 r_2 r_3 \right\} \right] e^{-2Z r_1} e^{-3Z(r_2 + r_3)/2} d\vec{V} .
 \end{aligned}$$

The disadvantage with these equations is that there is substantial cancellation among the separate integrals which appear. The advantage, of course, is that the separate integrals are of the type dealt with in the normalization integrals N^D and N^E and their approximate integration is considerably simpler than the integrations dealt with in $M_{n,e}^D$. Equations (5.28) and (5.29) were integrated by expanding out all the terms into a single poly-

nomial and treating each term individually. Because of the severe cancellation, the accuracy lost by combining terms such as $(r_2 + r_3)$ into one integral cannot be tolerated. This means that symmetry is lost in many of the integrals and the angles are evaluated by the necessary modification of Equations (5.22) and (5.23). Otherwise the technique is the same as used for N^D and N^E .

The results found for $M_{n,e}^D$ using Equations (5.28) and (5.5) are 0.01612 and 0.015745 respectively. These results furnish an internal test of our approximation technique. The cancellation involved in Equation (5.29) produces an answer which is 15 times smaller than the largest integrals appearing there. This magnifies the errors in the individual integrals by the factor, 15, if the errors are assumed uncorrelated. Now evaluating Equation (5.5) in the manner described above, the answer and the largest integral are about equal. There is then no magnification of the errors in the individual integral. Table II indicates that the errors in the approximation method applied to the normalization integrals, which appear in Equation (5.28), and to the perturbation integrals, which appear in Equation (5.5), are comparable in the range of Z for which we are interested. Thus a good measure of the error in $M_{n,e}^D$ as obtained by Equation (5.5) is simply the difference in the two results quoted divided by 15. This is an error of less than 0.2 % which compares quite favorably with the results of Table II for $Z = 3$.

Because of the good results found using Equation (5.28), M^E was evaluated by Equation (5.29). The small size of M^E renders the errors involved negligible for the accuracy we seek.

The terms $M_{e,e}^D$ and $M_{e,e}^E$ are quite small. Indeed for the particular problem at hand $M_{e,e}^E$ can be completely neglected. The terms in $M_{e,e}^D$ are evaluated with sufficient accuracy by taking the $\cos \theta_{k\ell, km}$ term completely outside the integral sign. Thus, for example,

$$\begin{aligned}
 (5.31) \quad & \int e^{-2Z(r_1 + r_2)} e^{-Zr_3} \cos \theta_{12, 31} \left(\frac{dE_1^2}{dr_{12}} (r_{12}) \right) \left(\frac{dE_1^2}{dr_{31}} (r_{31}) \right) \\
 & \times E_1^2(r_{23}) d\vec{V} \\
 & \cong C \left(\frac{dE_1^2}{dr_{31}} (r_{310}) \right) E_1^2(r_{230}) \int e^{-2Z(r_2 + r_3)} e^{-Zr_3} \\
 & \times \frac{dE_1^2}{dr_{12}} (r_{12}) d\vec{V}
 \end{aligned}$$

where

$$\begin{aligned}
 (5.32) \quad 2 \cos \theta_{12, 31} &= \frac{r_{12}^2 - r_{23}^2 + r_{31}^2}{r_{12} r_{31}} \\
 C &= \frac{\int \cos \theta_{12, 31} e^{-2Z(r_1 + r_2)} e^{-Zr_3} d\vec{V}}{\int e^{-2Z(r_1 + r_2)} e^{-Zr_3} d\vec{V}} .
 \end{aligned}$$

The integral in the numerator is evaluated with the formula

$$(5.33) \quad \int \cos \theta_{k\ell, km} d\Omega = 32\pi^3 \Theta_{k\ell} \Theta_{km} .$$

$d\Omega$ is the angular part of $d\vec{V}$ and the $\Theta_{k\ell}$ are defined in Equation (5.26). The subsequent radial integrations must be split properly and use made of Equation (5.27). In certain cases the Exponential Integral^[16] arises and the following properties are used in evaluating the subsequent integrals.

$$(5.34) \quad \int_x^\infty \frac{e^{-t}}{t} dt = -\text{Ei}(-x)$$

$$- \frac{d\text{Ei}(-x)}{dx} = \frac{e^{-x}}{x}$$

$$-\text{Ei}(-px) \xrightarrow{x \rightarrow 0} -0.577215 - \ln x - \ln p .$$

The expansion points and angles are treated in the same manner as described before.

6. Results

The energy calculated for the ground state of lithium as described in the previous section is -7.395 ± 0.005 A.U. The uncertainty in the energy value is due to the various approximations outlined. It should be noted that a given error in the individual integrations shows up in the

energy reduced by a factor of about three. The energy calculated here is compared in Table III with a number of other calculations using BWF formed from a product of symmetrized hydrogenic wave functions but with different numbers of variable parameters. These results can be obtained from the work of Wilson^[17].

The BWF with no variable parameters are the hydrogenic functions with $Z = 3$. Screening is then introduced through the variable parameters. With one variable parameter the inner and outer orbits are screened in the same way while with the two parameters they are screened individually and with three parameters the node in the outer orbit is adjusted independent of the screening. The seven parameter calculation of Huang, which introduced two of the three interelectron coordinates, and the experimental value^[18] are also given for reference.

Number of Parameters	Energy (A.U.)	
	BWF	SWF
0	- 7.057	- 7.395 \pm 0.005
1	- 7.289	
2	- 7.392	
3	- 7.418	
7	- 7.457	
Experimental	- 7.478	

TABLE III.

Comparison of various energy values calculated for the ground state of lithium.

The excellent result indicated in helium is fully realized in lithium. As in helium (see Table I), the SWF function is 5 times closer to the true answer than the zero order BWF. It is more than twice as close as the one parameter function and perhaps a little better than the two parameter function. The SWF, of course, has no adjustable parameters.

We can conclude that the Pluvillage approach is fully applicable to larger atomic systems. In addition, the mathematical approximation outlined can be extended without great difficulty to these atomic systems so that reasonably exact calculations could be carried out. This is especially true of quantities which might be calculated from the wave functions where errors of the order of 0.1% to 1% are tolerable. We also note that the approximation technique can be carried to higher orders, if necessary, to obtain requisite accuracy. This, however, would probably involve a considerable increase in labor.

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APPENDIX I

1. The integrals, I_n

The integral I_1 is given by Equation (2.20). Successive I_n values can be generated by differentiation. Thus, in view of Equation (2.19),

$$(I.1) \quad \frac{dI_n(Z)}{dZ} = - \frac{1}{2Z} I_{n+1}$$

By means of this formula and Equations (I.4) below, we arrive at the following expressions:

$$I_1 = \frac{E_1}{4Z^2} \left(\frac{1}{4Z^2} \right) \exp \left(\frac{1}{Z} \right)$$

$$I_2 = \frac{1}{4Z^2} \left[\frac{E_1}{2Z^2} + \frac{E_0}{Z} \right] \exp \left(\frac{1}{Z} \right)$$

$$I_3 = \frac{1}{8Z^3} \left[\left(2 + \frac{2}{Z} \right) \frac{E_1}{2Z^2} + \left(3 + \frac{2}{Z} \right) \frac{E_0}{Z} \right] \exp \left(\frac{1}{Z} \right)$$

$$I_4 = \frac{1}{16Z^4} \left[\left(6 + \frac{13}{Z} + \frac{4}{Z^2} \right) \frac{E_1}{2Z^2} + \left(12 + \frac{15}{Z} + \frac{4}{Z^2} \right) \frac{E_0}{Z} \right] \exp \left(\frac{1}{Z} \right)$$

$$I_5 = \frac{1}{32Z^5} \left[\left(24 + \frac{83}{Z} + \frac{52}{Z^2} + \frac{8}{Z^3} \right) \frac{E_1}{2Z^2} + \left(60 + \frac{108}{Z} + \frac{56}{Z^2} + \frac{8}{Z^3} \right) \frac{E_0}{Z} \right] \exp \left(\frac{1}{Z} \right)$$

$$I_6 = \frac{1}{64Z^2} \left[\left(120 + \frac{582}{Z} + \frac{555}{Z^2} + \frac{172}{Z^3} + \frac{16}{Z^4} \right) \frac{E_1}{2Z^2} \right. \\ \left. + \left(360 + \frac{840}{Z} + \frac{639}{Z^2} + \frac{180}{Z^3} + \frac{16}{Z^4} \right) \frac{E_0}{Z} \right] \exp \left(\frac{1}{Z} \right)$$

$$I_7 = \frac{1}{128Z^7} \left[\left(720 + \frac{4554}{Z} + \frac{5862}{Z^2} + \frac{2742}{Z^3} + \frac{512}{Z^4} + \frac{32}{Z^5} \right) \frac{E_1}{2Z^2} \right. \\ \left. + \left(2520 + \frac{7200}{Z} + \frac{7173}{Z^2} + \frac{2994}{Z^3} + \frac{528}{Z^4} + \frac{32}{Z^5} \right) \frac{E_0}{Z} \right] \exp \left(\frac{1}{Z} \right)$$

$$I_8 = \frac{1}{256Z^8} \left[\left(5040 + \frac{39672}{Z} + \frac{62602}{Z^2} + \frac{39945}{Z^3} + \frac{11328}{Z^4} + \frac{1424}{Z^5} + \frac{64}{Z^6} \right) \frac{E_1}{2Z^2} \right. \\ \left. + \left(20160 + \frac{63000}{Z} + \frac{81324}{Z^2} + \frac{45439}{Z^3} + \frac{12032}{Z^4} + \frac{1456}{Z^5} + \frac{64}{Z^6} \right) \right. \\ \left. \times \frac{E_0}{Z} \right] \exp \left(\frac{1}{Z} \right).$$

E_ν designates the modified Clifford-Bessel function of order, ν .
The argument in these functions in the above equations is $\frac{1}{4} Z^2$. E_ν has the following properties [12]

$$(I.3) \quad E_\nu(x) = \frac{J_\nu(2i\sqrt{x})}{(i\sqrt{x})^\nu}$$

$$= \sum_{n=0}^{\infty} \frac{x^n}{n!(\nu+n)!}$$

$$(I.4) \quad x E_{\nu+1} = E_{\nu-1} - \nu E_\nu$$

$$E_\nu' = E_{\nu+1}$$

$$x \frac{E_\nu'}{E_\nu} = \frac{E_{\nu-1}}{E_\nu} - \nu$$

The following recurrence relation [19] can also be used to obtain I_n :

$$(I.5) \quad 8Z^3 I_{n+2} = (12nZ^2 + 8Z) I_{n+1} - [6n(n+1)Z + 4n - 2] I_n$$

$$+ n(n-1)(n-2) I_{n-1}.$$

By using the recurrence relation higher I_n can be generated if only the three lowest I_n are known. This can be done quite rapidly on a desk calculator. However, accuracy is lost in evaluating the higher I_n by the recurrence relation and there is also a possibility of carrying along errors in the lower I_n . Values of I_n used in this paper were always computed by the explicit formulas (I.2) and the recurrence relation (I.5) and found identical within the accuracy desired (four significant figures). This served as an independent check on the correctness of the formulas in (I.2).

APPENDIX II

The alternate expression for $M_{n,e}$ is obtained by noting

$$(II.1) \quad \cos \theta_{1,1j} = \frac{1}{2} \frac{r_1^2 - r_j^2 + r_{1j}^2}{r_1 r_{1j}} = \frac{\partial r_{1j}}{\partial r_1}.$$

The derivative on the right is the partial of r_{1j} with respect to r_1 keeping r_j constant. Then

$$(II.2) \quad \frac{1}{2} \sum_{j \neq 1} \frac{r_1^2 - r_j^2 + r_{1j}^2}{r_1 r_{1j}} \frac{\partial}{\partial r_{1j}} = \frac{\partial}{\partial r_1}$$

where the derivation on the right applies to functions which depend explicitly on the r_{1j} alone. We can then convert certain derivatives with respect to the interelectron coordinates to derivatives with respect to the radial coordinates.

From Equations (3.6), (5.3) and the above

$$\begin{aligned}
 \text{(II.3)} \quad M_{n,e} &= \frac{1}{4} \sum_{i \neq j} \int \cos \theta_{i,ij} \frac{\partial}{\partial r_i} (D \prod_{\ell} \phi_{\ell}^2) \\
 &\quad \times \frac{\partial}{\partial r_{ij}} \left(\prod_{p > q} E_1^2(r_{pq}) \right) d\vec{V} \\
 &= \frac{1}{4} \sum_i \int \frac{\partial}{\partial r_i} (D \prod_{\ell} \phi_{\ell}^2) \frac{\partial}{\partial r_i} \left(\prod_{p > q} E_1^2(r_{pq}) \right) d\vec{V}.
 \end{aligned}$$

The term $\phi_m(r_{\ell})$ has been abbreviated to ϕ_{ℓ} and D indicates the Slater determinant of the functions immediately following this symbol. The second equation in (II.3) can now be integrated by parts, by explicitly expressing r_{pq} in terms of \vec{r}_p, \vec{r}_q . The boundary terms drop out in the integration by parts, leaving

$$\begin{aligned}
 \text{(II.4)} \quad M_{n,\ell} &= -\frac{1}{4} \sum_i \int (\prod E_1^2) \frac{\partial}{\partial r_i} \left[r_i^2 \frac{\partial}{\partial r_i} (D \prod_{\ell} \phi_{\ell}^2) \right] \\
 &\quad \times \prod_j dr_j \sin \theta_j d\theta_j d\phi_j \\
 &= -\frac{1}{2} \sum_i \int (\prod E_1^2) D \left[\left(\prod_{\ell} \phi_{\ell} \right) \frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \frac{\partial \prod \phi_{\ell}}{\partial r_i} \right) \right. \\
 &\quad \left. + 2 \sum \frac{\partial \prod \phi_{\ell}^2}{\partial r_i} \right] d\vec{V}.
 \end{aligned}$$

The argument in the E_1 's has been suppressed for convenience. From Equation (II.4), the Schroedinger Equation:

$$\frac{1}{r_1^2} \frac{\partial}{\partial r_1} (r_1^2 \phi_1) = (E_1 - \frac{Z}{r_1}) \phi_1$$

and the form for the wave function given by Equation (5.1), the expressions (5.28) and (5.29) follow.

* * *

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Research Reports and Publications

The following is a list of all research reports in the CX series.

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CX-36	H. Moses and S.F. Tuan	Potentials With Zero Scattering Phase	Nov., '58
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CX-38	S.I. Rubinow and J.B. Keller	Asymptotic Solution of Eigenvalue Problems	Feb., '58
CX-39	S.I. Rubinow	Effective Two-Body Method for Two-Electron Atoms	Feb., '59
CX-40	L. Spruch and L. Rosenberg	Low Energy Scattering by a Compound System: Positrons on Hydrogen	Feb., '59

Publications Not Based on Reports

S. Borowitz and B. Friedman	Three-Body Scattering Problems Phys. Rev., <u>93</u> , 251 (1954).
S. Borowitz	Electron-Ion Recombination at Low Pressures Trans. AIEE, <u>72</u> , Part I, 430 (1953).
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41 Walsh & Borowitz.

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**N. Y. U. Institute of
Mathematical Sciences**

25 Waverly Place
New York 3, N. Y.

